A Study on Degradation of Azo Dyes Present in Industrial Effluent in Meerut Region

Synopsis submitted to IIMT UNIVERSITY in partial fulfillment of the requirements for the award of the Degree of

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By

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Part time

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DECLARATION

The research work embodied in this synopsis entitle **"A Study on Degradation of Azo Dyes Present in Industrial Effluent in Meerut Region"** will be carried out in the laboratory of Department of Chemistry, School of Basic sciences & Technology, IIMT University, Meerut. The work is original and has not been submitted in part or full for any degree or diploma of this or any other University.

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1. Introduction

The demand of energy is increasing day by day due to the increase of industrialization and population. In near future world will require two time to the current supply of its energy till 2050. At present time most of the energy demand is fulfilled by the use of fossil fuels like Petroleum, Coal, Natural gas etc. which is depleting day by day. Beside that the use of fossil fuels are producing pollutants which are harmful for environment. The industries like textile, paper, printing and leather uses different types of chemical compounds. These chemical compounds are further come out as industrial effluents in the water bodies and cause serious water pollution.

Dyes are colored compounds which are used to impart color through binding chemically with the substrate. They can be either natural or synthetic dyes. The synthetic dyes are frequently used in the textile, paper, printing and leather industries which are harmful for human health. These dyes cause serious problem to the aquatic inhabitants as dyes stop the sunlight to penetrate into water which inhibit the growth of aquatic animals and plant. The natural dyes are comparatively less hazardous but the mordant which are used to fix the color of dye are harmful and cause serious environmental and health problems.

There are several techniques which are used to degrade the dyes present in the water. It includes chemical methods, physical methods, biological methods and their combinations. In chemical methods commonly activated carbon is used which can absorb dye from water but this method is useful only at small scale and when we move on industrial scale it get failed due to high cost and long time. In biological methods micro-organisms are used to degrade dyes but these methods require strict temperature and pH control which is very difficult at industrial scale. In physical methods coagulation, flocculation and reverse osmosis is used which are also very

costly and time taking. Beside that these methods can generate several secondary pollutants. In photo-catalytic methods sun light is used in the presence of a photo-catalyst to degrade dyes. This method is comparatively less costly because it is required in less quantity and it is not consumed in the reaction and we can use it several times. Beside that no harmful by products are formed in this process.

2. Literature Review

The increase of industrialization also increases the need of energy. At present time most of the energy demand is fulfilled by the use of fossil fuels like Petroleum, Coal, Natural gas etc. which is depleting day by day and also causing pollution. It increases the need of new environmental friendly sources of energy for sustainable future. It draws the focus of researchers towards photo catalyst which can open the new horizons in the field of energy production. The semiconductor based photo catalyst can use to harvest the solar energy and use it in the water splitting into H_2 and O_2 gas, Photo reduction of CO_2 into hydrocarbons, Degradation of several pollutants and also synthesis of organic compounds.

In 1972, Fujishima and Honda carried out water splitting in presence of UV light by the use of TiO_2 electrode [1]. It is the path breaking study in the field of Photo catalysis. In 1979 Inoue and coworkers study the photo reduction of CO2 into several hydrocarbons by using several semiconductor powders such as TiO_2, ZnO, SiC, GaP and CdS in aqueous solution [2]. Since then several studies has been carried out by different scientific groups in the field of Photo catalyst like TiO_2, ZnO, Fe_2O_3, CdS, $BiWO_6$, $BiVO_4$ etc.

Later on researchers focus their interest on the visible light responsive photo catalyst as visible light is the large fraction of solar light spectrum. However the large band gap energy of traditional semiconductors like TiO_2 makes him less responsive towards visible light. Therefore

in search of new visible light responsive catalyst, graphitic carbon nitride draws the focus of research community due to its lower band gap, high physiochemical stability and earth abundant nature.

Graphitic Carbon Nitride is nitrogen rich polymer made up by the thermal polymerization of several precursors like Melamine, Cynamide, Dicyndiamide, Urea, Thiourea and Ammonium thiocynate etc. C_3N_4 has seven phases among them tri-s triazine based g-C_3N_4 is most stable and energetically favored. Tri-s-triazine (heptazine) is the basic unit and building block of the g-C_3N_4. It has polymeric structure due to which it is easy to modulate the surface chemistry of g-C_3N_4 by surface engineering to get the favorable results. In comparison with TiO2, g-C_3N_4 has lower band gap, higher stability and lower cost but it also have higher recombination rate of charge carriers, low electrical conductivity and low absorption above 460nm. Due to which bare g-C_3N_4 is not practically useful as photo catalyst and there are several modification requires in bare g-C_3N_4 including synthesis modification, electronic structure modulation and nanostructure designing is required. There are several other strategies which can be applied to enhance the photo catalytic properties of g-C_3N_4 like doping of metals and non metals, use of co-catalyst, preparation of hetero-junction with other materials etc.

3. Types of Pollutants Discharged from Industries in Meerut Region

Meerut is a major city of western part of Uttar Pradesh. It is only 70 Km distant from the national capital New Delhi. It is developing as the major industrial centre of Western Uttar Pradesh. It is mainly famous for sports and sugarcane industries. But in recent time several other Industries like paper industry, leather industry and pharmaceutical industry are also developed in Meerut. This industrial development has brought a significant increase in the infrastructural development and also generates employment. Beside that it also cause several environment

related problems. These industries make the air quality worsen and also dump lots industrial effluents in the water bodies which cause serious environmental problem [3]. It can cause serious health problems when such contaminated water is consumed by human beings. Beside that such contaminated water can cause the danger to the aquatic animal and plants. These industrial effluents include several organic matters, polymers, heavy metals [4], dyes etc. The category and type of pollutants mainly depends on the type of industry from which the effluent discharged [5]. The aim of present study is mainly focus on dyes which is the main constituent of the effluents discharged from paper, leather and textile industry.

4. What is dye?

Dyes are color substances which are used to impart color in the materials. Dyes can be organic or inorganic compound which can absorb the visible range of light due to which they appear colored. They are commonly used in textile, leather, paper and food industries. These industries used lots of water for dyeing process according to Kant et. al (2012) the daily water consumption of an average size textile mill is 1.6 million liters. According to a study around 8000 types of chemicals used for the dyeing process and around 80% of dye would remain on the textile fabric while other 20% go up in drains.

Azo dyes is a group of dye which have azo (-N=N-) group present as chromophore. It is a group of synthetic aromatic dye which may have one or more azo groups [6]. It is a group of dye which is used at large level in textile industries [6, 7]. However it is also used in leather industry, paper industry, paint industry and several other industries as coloring agent.

Beside dyes there are several other compounds like chlorine is used in these industries which are carcinogenic in nature. There are some metal oxides which are called mordant used to fix the

color of dyes. When these industrial effluents with water came out from industries, it carries lots of dye and other chemical compounds which are harmful to human health as well as for aquatic animals. Beside that these industries also cause air pollution through emitting the harmful gases, soil pollution by sludge came out from factories and noise pollution by the noise of heavy machineries.

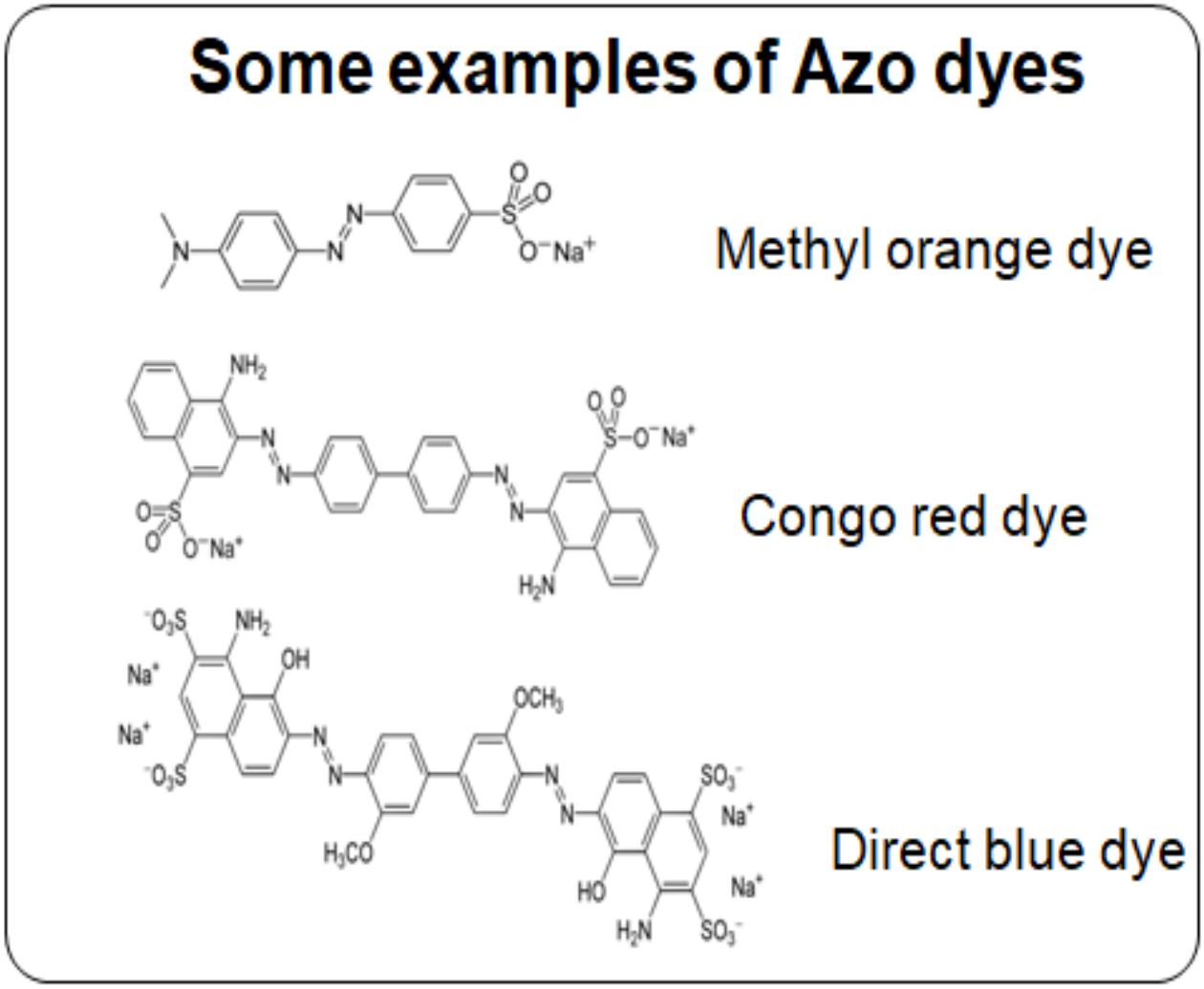

Figure 1: Some examples of azo dyes.

5. Consequences of Dyes Pollution in Water

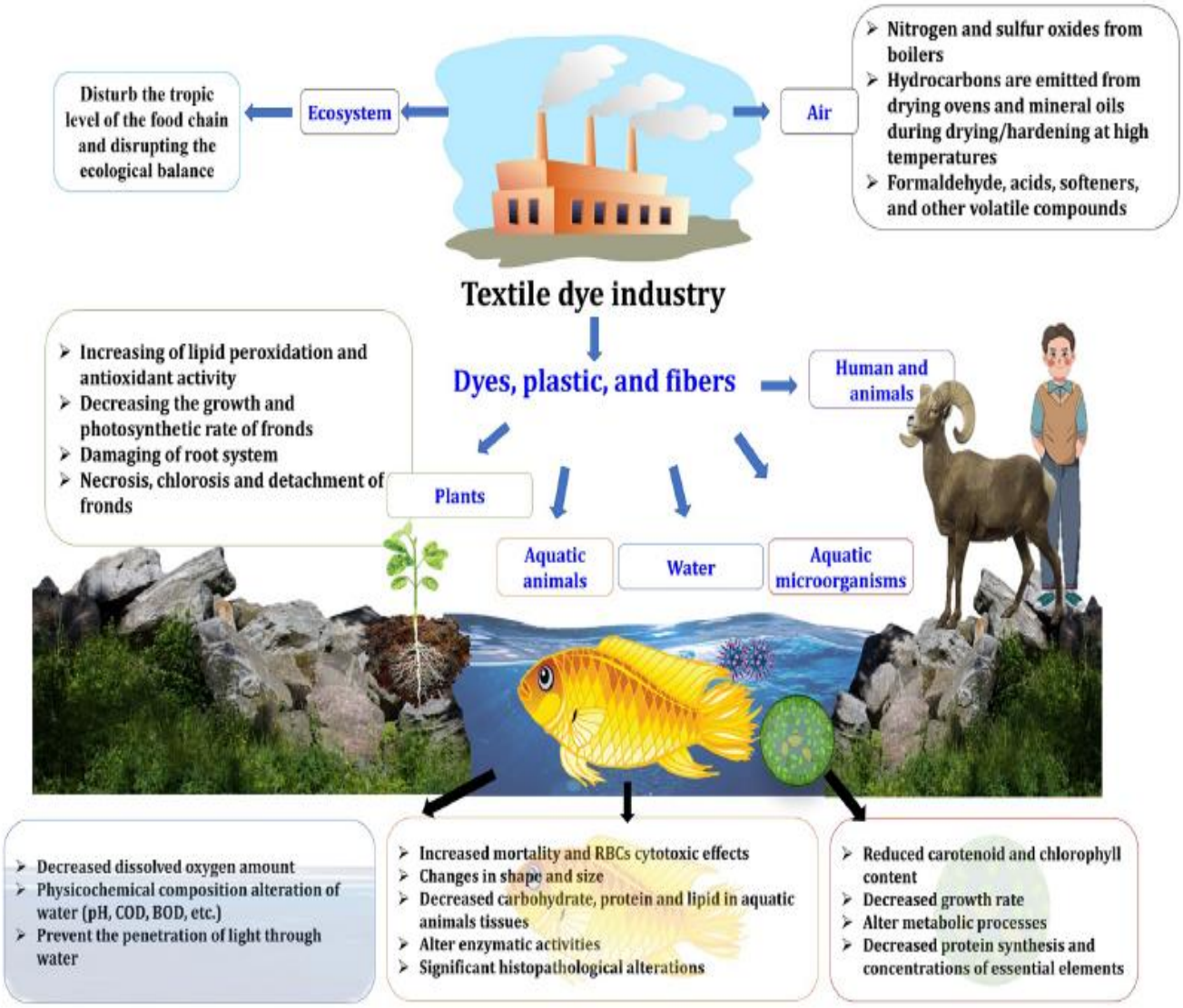
Disturb the tropic level of the food chain and disrupting the ecological balance
Ecosystem
Air
Nitrogen and sulfur oxides from boilers
Hydrocarbons are emitted from drying ovens and mineral oils during drying/hardening at high temperatures
Formaldehyde, acids, softeners, and other volatile compounds
Textile dye industry
Dyes, plastic, and fibers
Human and animals
Increasing of lipid peroxidation and antioxidant activity
Decreasing the growth and photosynthetic rate of fronds
Damaging of root system
Necrosis, chlorosis and detachment of fronds
Plants
Aquatic animals
Water
Aquatic microorganisms
Decreased dissolved oxygen amount
Physicochemical composition alteration of water (pH, COD, BOD, etc.)
Prevent the penetration of light through water
Increased mortality and RBCs cytotoxic effects
Changes in shape and size
Decreased carbohydrate, protein and lipid in aquatic animals tissues
Alter enzymatic activities
Significant histopathological alterations
Reduced carotenoid and chlorophyll content
Decreased growth rate
Alter metabolic processes
Decreased protein synthesis and concentrations of essential elements

Figure 2: Affects of textile dye industry pollutants on the ecosystem [4].

Industry waste contain dyes, organic compounds sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, chromium compounds and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt which collectively make the effluent highly toxic [8]. The color present in effluent make the water source turbid or colored which make the penetration of sun light difficult, it is very harmful for water bodies. The chemical present in the industrial effluent have lots of chemicals which change the pH and affect the BOD and COD value of water source and make the survival of water living animals difficult. The effluents contain several chemicals

like organic compounds and heavy metals which cause harmful effect in aquatic plants, micro-organisms, animals and human being [4].

The color of dye make the water turbid which restricts the penetration of sun light into water that resists the photo-synthesis in aquatic plants which is very harmful for them. That changes the chemical composition of water and affects the water ecosystem in a bad manne [9]. The azo dyes are synthetic aromatic compounds which gave aromatic ammine [10] by degradation that are carcinogenic in nature and cause harmful effect on aquatic animals [11]. The studies show that azo dye cause problem in the gills, liver, kidney, gut and other vital organs of the aquatic animals [7, 12] . The dye and other chemical compounds present in industrial effluents came into human body by the consumption of polluted water and aquatic animals. The studies shows that these dye pollutants contain lot of carcinogenic agents which cause several type of cancer in human being [13, 14] , beside that these pollutants also impact the skin , liver, kidney, nervous system, reproductive system, enzymatic system, human chromosome and several other vital organs of human being [7, 12, 15] .

6. Strategy to Overcome Dye Pollution

There are several methods used for the degradation of dyes presents in the industrial effluent. These methods can be broadly classified into biological methods, physical methods and chemical methods. However, only one method is not sufficient, therefore the combination of two or more techniques is applied to remove dyes and other pollutants completely. The method applied on a particular dye depends on the structure and the nature of the dye. The biological degradation of dyes can be classified into aerobic and anaerobic biodegradation. Aerobic degradation is catalyzed by specific enzyme like azo reductase enzyme for azo dyes [15]. Then it is treated with

some microorganisms which degrade complex dyes into intermediate metabolites which can further degrade by using other micro-organism. Anaerobic degradation is comparative simple and non specific method [16]. This method is applied in the absence of oxygen and enzymes are used as catalyst to reduce the dyes. These reduction reactions are carried out in the presence of certain co-factors and reduction mediators. In biological degradation several types of microorganisms like bacteria, fungi, yeast, and actinomycetes are used [10, 17]. The biological methods have a problem that they required a specific temperature and pH to work which is quite difficult to maintain.

The physical methods include adsorption, ion exchange, filtration, coagulation, flocculation, reverse osmosis etc. These methods are quite easy and nonspecific but the problems with these methods are that they are quite time taking, expensive and also producing sludge as secondary pollutants [18]. Due to which these methods are not applicable at industrial level.

In chemical techniques there are several types of methods are used but the most common techniques are Fenton reagent technique, ozonolysis and photo-catalytic method [19]. The problem with the conventional chemical techniques is that they required expensive chemicals and they produce several secondary pollutants which are further harmful of environment.

7. Why Photo- catalytic Degradation

Photo catalytic degradation is processes in which dyes and other pollutants are degrade in the presence of a photo-catalyst with the use of sun light. Photo catalytic degradation is cost effective as the catalyst used in the process is reusable as it is not consumed in the reaction. Beside that this method does not require heavy instrumental setup and it produce no secondary

pollutants. In photo catalytic degradation, oxidation or reduction of dyes and other pollutants is carried out on the surface of semiconductor based photo catalyst. In this process these pollutants converts into less hazardous simple molecules.TiO_2 is the most common photo catalyst which is used in the degradation of dyes however it has a problem that is absorb UV radiation which is only a small fraction of sun light. So several other photo catalysts like g-C_3N_4 came in picture which is able to absorb visible light but it is less reactive than TiO_2. The solution of this problem came with the structure modification of photo catalyst and with the formation of hetero junction [20]. The selection of photo catalyst for degradation of dyes depends on several factors like efficiency of photo catalyst, stability of photo catalyst, band gap, conductivity etc. [21]. Beside that cost of material is also an important factor at industrial level. There are several other factors like pH, initial concentration, intensity of light and catalyst load also effect the rate of dye degradation [21, 22].

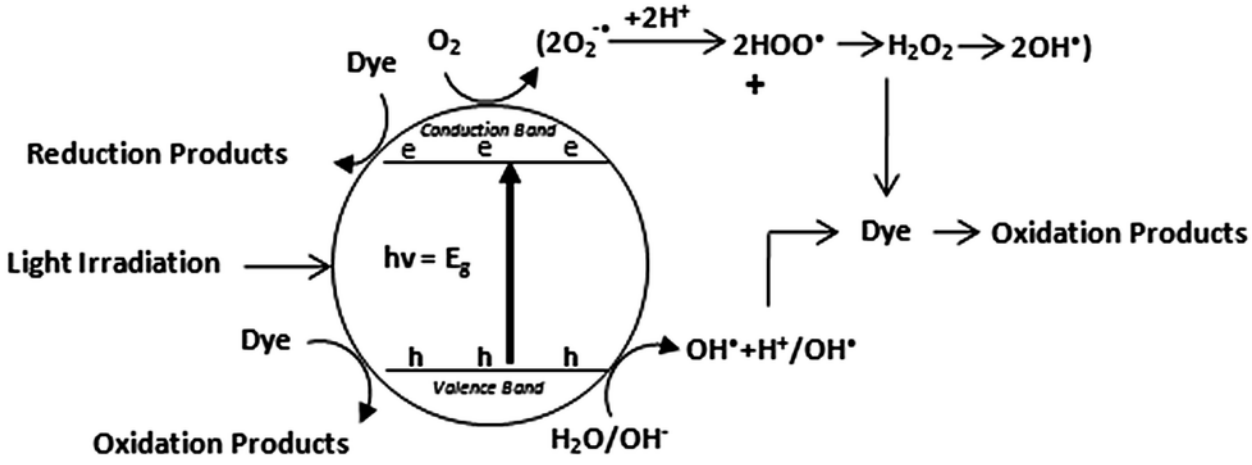

Figure 3: Mechanism of photo-catalytic degradation of dyes [23].

The photo catalytic degradation of dyes is considered to be pseudo first order reaction [24]. The reaction involves electronic transition from valance band to conduction band by absorption of sun light which generated photo-generated electrons in conduction band and holes in valance

band. These photo-generated electrons and holes facilitate the production of super oxides and hydroxide radicals by reduction and oxidation of O_2 and H_2O respectively [24]. These species have capacity to degrade the dyes and other pollutants by oxidation. In the other way If photo catalytic degradation is coupled with electrochemical method, it became more effective [25]. So we can easily understand that photo catalytic degradation is better than other conventional methods of dye degradation.

8. Objectives of the Present Work:

- To identify the azo dyes pollutants present in the industrial effluent in Meerut region.
- To identify the most suitable photo-catalyst for the photo degradation of azo dyes.
- Photocatalytic degradation/mineralization of azo dyes present in the industrial effluent.

References:

[1] A. Fujishima and K. Honda, "Electrochemical Photolysis of Water at a Semiconductor Electrode," *Nature*, vol. 238, no. 5358, Art. no. 5358, Jul. 1972, doi: 10.1038/238037a0.

[2] T. INOUE, A. FUJISHIMA, S. KONISHI, and K. HONDA, "Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders," *Nature*, vol. 277, no. 5698, pp. 637–638, Feb. 1979, doi: 10.1038/277637a0.

[3] S. Singh, R. Tiwari, and R. Pandey, "Water Pollution due to Discharge of Industrial Effluents with special reference to Uttar Pradesh, India – A review," Dec. 2018.

[4] C. K. Jain, D. C. Singhal, and M. K. Sharma, "Metal Pollution Assessment of Sediment and Water in the River Hindon, India," *Environ. Monit. Assess.*, vol. 105, no. 1, pp. 193–207, Jun. 2005, doi: 10.1007/s10661-005-3498-z.

[5] S. Suthar, J. Sharma, M. Chabukdhara, and A. K. Nema, "Water quality assessment of river Hindon at Ghaziabad, India: impact of industrial and urban wastewater," *Environ. Monit. Assess.*, vol. 165, no. 1, pp. 103–112, Jun. 2010, doi: 10.1007/s10661-009-0930-9.

[6] S. Sarkar, A. Banerjee, U. Halder, R. Biswas, and R. Bandopadhyay, "Degradation of Synthetic Azo Dyes of Textile Industry: a Sustainable Approach Using Microbial Enzymes," *Water Conserv. Sci. Eng.*, vol. 4, no. 2, pp. 121–131, Sep. 2017, doi: 10.1007/s41101-017-0031-5.

[7] R. Al-Tohamy *et al.*, "A critical review on the treatment of dye-containing wastewater: Ecotoxicological and health concerns of textile dyes and possible remediation approaches for

environmental safety," *Ecotoxicol. Environ. Saf.*, vol. 231, p. 113160, Feb. 2022, doi: 10.1016/j.ecoenv.2021.113160.

[8] R. Kant, "Textile dyeing industry an environmental hazard," *Nat. Sci.*, vol. 04, no. 01, pp. 22–26, 2012, doi: 10.4236/ns.2012.41004.

[9] M. Berradi *et al.*, "Textile finishing dyes and their impact on aquatic environs," *Heliyon*, vol. 5, no. 11, p. e02711, Nov. 2019, doi: 10.1016/j.heliyon.2019.e02711.

[10] A. Pandey, P. Singh, and L. Iyengar, "Bacterial Decolorization and Degradation of Azo Dyes," *Int. Biodeterior. Biodegrad.*, vol. 59, pp. 73–84, Mar. 2007, doi: 10.1016/j.ibiod.2006.08.006.

[11] E. Van Ael, A. Covaci, R. Blust, and L. Bervoets, "Persistent organic pollutants in the Scheldt estuary: environmental distribution and bioaccumulation," *Environ. Int.*, vol. 48, pp. 17–27, Nov. 2012, doi: 10.1016/j.envint.2012.06.017.

[12] B. de C. Ventura-Camargo, "Azo Dyes: Characterization and Toxicity– A Review," Jan. 2013, Accessed: Oct. 11, 2022. [Online]. Available: https://www.academia.edu/30221458/Azo_Dyes_Characterization_and_Toxicity_A_Review

[13] K.-T. Chung, "Azo dyes and human health: A review," *J. Environ. Sci. Health Part C Environ. Carcinog. Ecotoxicol. Rev.*, vol. 34, no. 4, pp. 233–261, Oct. 2016, doi: 10.1080/10590501.2016.1236602.

[14] E. Clonfero, P. Venier, M. Granella, and A. G. Levis, "[Leather azo dyes: mutagenic and carcinogenic risks]," *Med. Lav.*, vol. 81, no. 3, pp. 222–229, Jun. 1990.

[15] J. Feng, C. E. Cerniglia, and H. Chen, "Toxicological significance of azo dye metabolism by human intestinal microbiota," *Front. Biosci. Elite Ed.*, vol. 4, no. 2, pp. 568–586, Jan. 2012, doi: 10.2741/e400.

[16] Y. Gao, B. Yang, and Q. Wang, "Biodegradation and Decolorization of Dye Wastewater: A Review," *IOP Conf. Ser. Earth Environ. Sci.*, vol. 178, p. 012013, Aug. 2018, doi: 10.1088/1755-1315/178/1/012013.

[17] Y. Patel, U. Chhaya, D. Rudakiya, and S. Joshi, "Biological Decolorization and Degradation of Synthetic Dyes: A Green Step Toward Sustainable Environment," 2021, pp. 77–110. doi: 10.1007/978-981-15-7455-9_4.

[18] R. L. Singh, P. K. Singh, and R. P. Singh, "Enzymatic decolorization and degradation of azo dyes – A review," *Int. Biodeterior. Biodegrad.*, vol. 104, pp. 21–31, Oct. 2015, doi: 10.1016/j.ibiod.2015.04.027.

[19] R. V. Kandisa and N. Saibaba KV, "Dye Removal by Adsorption: A Review," *J. Bioremediation Biodegrad.*, vol. 07, no. 06, 2016, doi: 10.4172/2155-6199.1000371.

[20] W.-J. Ong, L.-L. Tan, Y. H. Ng, S.-T. Yong, and S.-P. Chai, "Graphitic Carbon Nitride (g-C3N4)-Based Photocatalysts for Artificial Photosynthesis and Environmental Remediation: Are We a Step Closer To Achieving Sustainability?," *Chem. Rev.*, vol. 116, no. 12, pp. 7159–7329, Jun. 2016, doi: 10.1021/acs.chemrev.6b00075.

[21] M. Mohd Nazri and N. Sapawe, "A short review on photocatalytic toward dye degradation," *Mater. Today Proc.*, vol. 31, Feb. 2021, doi: 10.1016/j.matpr.2020.10.967.

[22] H. Anwer, A. Mahmood, J. Lee, K.-H. Kim, J.-W. Park, and A. C. K. Yip, "Photocatalysts for degradation of dyes in industrial effluents: Opportunities and challenges," *Nano Res.*, vol. 12, no. 5, pp. 955–972, May 2019, doi: 10.1007/s12274-019-2287-0.

[23] M. A. Rauf and S. S. Ashraf, "Fundamental principles and application of heterogeneous photocatalytic degradation of dyes in solution," *Chem. Eng. J.*, vol. 151, no. 1–3, pp. 10–18, 2009.

[24] B. Viswanathan, "Photocatalytic Degradation of Dyes: An Overview," *Curr. Catal.*, vol. 07, Dec. 2017, doi: 10.2174/2211544707666171219161846.

[25] Md. M. Islam and S. Basu, "Effect of morphology and pH on (photo)electrochemical degradation of methyl orange using TiO2/Ti mesh photocathode under visible light," *J. Environ. Chem. Eng.*, vol. 3, no. 4, Part A, pp. 2323–2330, Dec. 2015, doi: 10.1016/j.jece.2015.08.026.